TITLE: INVESTIGATION OF MIXED METAL SORBENT/CATALYSTS FOR THE SIMULTANEOUS REMOVAL OF SULFUR AND NITROGEN OXIDES

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ABSTRACT

OBJSECTIVE

The objective of this research project is to conduct kinetic and parametric studies of SCR of NO_x with NH_3 and CH_4 over alumina-supported ceria and copper oxide-ceria sorbent/catalysts; investigate SO_2 removal at lower temperatures by supported copper oxide-ceria sorbents; and investigate the possibility of elemental sulfur production during regeneration with CO or with CH_4-air mixtures.

ACCOMPLISHMENTS TO DATE

Significant work was done by the investigators on the cerium oxide-copper oxide based sorbent/catalysts for the combined removal of sulfur and nitrogen oxides from the flue gases of stationary sources. A relatively wide temperature window was established for the use of alumina supported cerium oxide-copper oxide mixtures as regenerable sorbents for SO_2 removal.

In the 723-823 K temperature range combined cerium oxide-copper oxide sorbents have specific sorbent capacities (mass of sulfur removed per unit mass of metal sorbent) and sulfation rates significantly larger than those of cerium oxide or copper oxide sorbents used alone. Best sulfation performance was shown by the sorbent containing 1:1 molar ratio of cerium and copper. Specific sulfur capacities decreased as the coverage of the support surface by the metal oxides approached monolayer coverage. Sorbents appeared to be resistant to cycling. No loss of sulfation capacity was observed after the third cycle.

Preliminary evaluation of these sorbents as catalysts for the selective reduction of NO_x gave promising results with ammonia, but indicated low selectivity when methane was used as the reductant. The catalyst containing equimolar amounts of Ce and Cu is not active for NO reduction by CH_4 at low temperatures and is not selective at high temperatures. It is active and selective for NO_2 reduction with

CH_4 at temperatures below 423 K. and it is active and selective for NO_2 reduction with NH_3 at temperatures 373 K to 733 K. In the reduction of NO with NH_3, the conversion passes through a maximum at 573 K.

Different catalyst compositions and reaction conditions are currently being investigated for the reduction of NO and NO_2 with methane and ammonia.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

Air pollution arising from the emission of sulfur and nitrogen oxides as a result of combustion taking place in boilers, furnaces and engines, has increasingly been recognized as a problem. Simultaneous removal of SO_2 and NO_x using a regenerable solid sorbent will constitute an important improvement over the use of separate processes for the removal of these two pollutants from stack gases and possibly eliminate several shortcomings of the individual SO_2 and NO_x removal operations. This process will allow simple and reliable cleanup of large volumes of stack gases at a competitive cost; produce a concentrated stream of SO_2 which can easily be converted into valuable by-products; and eliminate the waste materials generated in some other sulfur removal processes. Thus, post-combustion NO_x removal may become economical even for small-scale combustors if it can be combined with SO_2 clean-up. Department of Energy's Pittsburgh Energy Technology Center (PETC) has been involved with the development of a regenerative fluidized bed process using copper oxide-impregnated alumina spheres for simultaneous removal of SO_2 and NO_x since late 1960's. More recent studies at PETC considered cerium oxide as an alternate sorbent to CuO.

The proposed research involves the elimination of gaseous pollutants arising from coal utilization. It is expected that it will constitute a step in the commercial application of a new technology for the simultaneous removal of SO_2 and NO_x.

PLANS FOR THE COMING YEAR

- Complete the SCR studies with all the prepared catalyst samples at different temperatures and gas compositions.
- Investigate the regeneration of sorbent with CO and the possibility of elemental sulfur production.
- Evaluate the data.
- Write the final report.

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Journal Articles (peer reviewed)

1. Akyurtlu, J. F., and Akyurtlu, A.,: "Behavior of Ceria-Copper Oxide Sorbents under Sulfation Conditions", accepted for publication at **Chem. Eng. Sci**. (ISCRE Issue), December 1998.

Conference Presentations

1. Akyurtlu, A. and Akyurtlu, J. F., "Supported Ceria Sorbents for Combined Removal of SO_2 and NO_x from Flue Gases: Sulfation Characteristics and Effect of Ammonia on Sulfation", presented at the 15th Meeting of the North American Catalysis Society at Chicago, IL, May 18-22, 1997.

2. Akyurtlu, J. F. and Akyurtlu, A.: "Simultaneous Removal of SO_2 and NO_x from Flue Gases by Ceria Sorbents", presented at the EPRI-DOE-EPA Combined Utility Air Pollutant Control Symposium (MEGA Symposium), Washington, D.C., August 25-29, 1997.
3. Akyurtlu, A., and Akyurtlu, J. F., "Investigation of Mixed Metal Sorbent/Catalysts for the Simultaneous Removal of Sulfur and Nitrogen Oxides", presented at the UCR Contractors' Review Conference, at Pittsburgh, PA, on June 2, 1998.
4. Akyurtlu, A., and Akyurtlu, J. F., "Behavior of Ceria-Copper Oxide Sorbents under Sulfation Conditions", presented at the 15th International Symposium on Chemical Reaction Engineering (ISCRE 15), at Newport Beach, CA, on September 13-16, 1998.
5. Akyurtlu, J. F., and Akyurtlu, A., "Supported CuO/CeO_2 Sorbents for Gas Cleaning in Power Generation Systems", presented at the 15th Annual International Pittsburgh Coal Conference at Pittsburgh, PA, September 14-18, 1998. It has also been published in the Conference Proceedings.
6. Akyurtlu, A., and Akyurtlu, J. F., "Behavior of Supported Ceria/CuO Sorbents under Sulfation Conditions", presented at the Session 62 of the 2nd World Congress on Environment held at Miami Beach, FL in November 15-19 1998.
7. Akyurtlu, A., and Akyurtlu, J. F., "Investigation of Supported Ceria-Copper Oxide Sorbents for the Removal of SO_2 and NO_x from Flue Gases", presented at the DOE 1999 Seventh Annual Historically Black Colleges and Universities and Other Minority Institutions, Miami, FL, March 16-18, 1999.

Students Supported Under This Grant

- John McHugh, undergraduate chemical engineering student (graduated December, 1997).
- Courtney Ammritt, undergraduate chemical engineering student (will graduate May, 1999).
- Franklin Julien, undergraduate chemical engineering student.
- Burnitta Johnson, undergraduate chemical engineering student.
- Joshua Valentine, undergraduate chemical engineering student.
- Amy Beyer, undergraduate chemical engineering student.
- Takeila Battle, undergraduate chemical engineering student.